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TECHNICAL REPORT PC-1

STUDIES OF AN OXYGEN ELECTRODE

for

A LONG-LIFE PRIMARY CELL

U. S. Navy Contract No. NOnr 835(00)

Sponsored by ONR, Chemistry Branch

Submitted by:

Michael McCarthy, Project Engineer
Ralph Bloom, Jr., Project Supervisor

Approved by:

Noah S. Davis, Jr., Manager
Special Projects Division

BUFFALO ELECTRO-CHEMICAL COMPANY, INC.

Station B Buffalo 7, N. Y.

1 May 1953

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Table of Contents

I. INTRODUCTION

The Buffalo Electro-Chemical Company, Inc. is investigating the use of H_2O_2 in a long life primary cell under a contract with the Office of Naval Research. At the outset of this investigation, it was decided that there were two possible cells to be considered. The first would utilize the oxygen from external decomposition of H_2O_2, and the second would utilize the H_2O_2 directly.

The oxygen electrode characteristics under normal conditions of temperature and pressure were well known and the oxygen electrode is commercially available in the National Carbon Co. air cells. The development of an H_2O_2 electrode on the other hand has never been accomplished. The theoretical capacity of a cell utilizing an H_2O_2 electrode; however, is such that an attempt to develop this electrode was desirable. Such a cell would utilize the heat of decomposition of the H_2O_2 directly; whereas, this energy would be lost in a cell utilizing the oxygen only. In this case, the lost energy could be recovered by utilizing the H_2O_2 decomposition products in a turbine prior to supplying the oxygen portion to the cells. In addition, a cell which would develop power with reasonable efficiency on either oxygen or air would be suitable for a dual operating propulsion system.

The first phase of the work; therefore, consisted of a study of the use of the oxygen from H_2O_2 in a National Carbon air cell and, in particular, a study of the effect of elevated temperature and increased electrolyte concentration on the performance of this cell. It is this phase that has been completed and is reported herein.

II. Theoretical Considerations

The theoretical oxygen electrode reaction in an alkaline cell is:

$$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^- \quad E^\circ_3 = .401$$

In an acid oxygen cell, it would be:

$$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O \qquad E^\circ = 1.229$$

In practice these reactions are never obtained. The oxygen actually forms Hydroxide and Perhydroxyl ions according to the reactions:

In alkaline: $O_2 + H_2O + 2e^- \longrightarrow OH^- + HO_2^- \qquad E^\circ_B = -.076$

In acid: $O_2 + 2H^+ + 2e^- \longrightarrow H_2O_2 \qquad E^\circ = .682$

The perhydroxyl ion then decomposes forming OH^- and O_2.

Commercial air cells, consisting of porous carbon electrodes combined with metallic zinc electrodes, are run in strongly alkaline electrolytes. The decrease in voltage of the oxygen electrode from .682 to -.076 volts is made up by an increase in the potential of the zinc electrode which reacts as follows:

In alkaline: $Zn + 4OH^- \longrightarrow ZnO_2^{=} + 2H_2O + 2e^- \qquad E^\circ_B = 1.216$

In acid: $Zn \longrightarrow Zn^{++} + 2e^- \qquad E^\circ = .763$

III. SCOPE OF WORK

As originally set up, the work on oxygen cells was divided into two parts:

1. Study of the operation of National Carbon air cells with oxygen at various temperatures and with varying electrolyte concentrations.
2. Investigation of porous metals in place of porous carbon for oxygen electrodes.

Work on Part 2 was barely started before the O_2 electrode work was dropped in favor of a more intensive investigation of the possibilities of an H_2O_2 cell. Three porous metal electrodes were tried. Porous stainless steel was unsatisfactory because of the formation of an inert and insulating oxide film. Porous

copper (in the form of an Oilite bronze material) also formed an oxide film, but this acted as a depolarizer in the same manner as a copper oxide depolarized cell. Because of the low open circuit voltage of this cell (about 0.9 volts), work on the copper electrode was dropped. One preliminary test on a porous Nickel electrode indicated that this material was satisfactory in hot electrolyte (test was run between 110 and 150°C). This merely confirmed the work of others with Nickel electrodes.

The bulk of the work done by the Buffalo Electro-Chemical Company on oxygen cells has been with the National Carbon CG500 air cell electrode. Several tests were [illegible] the AC500 air cell electrode while the test set up and the operating procedure were being developed. About this time, the CG500 electrode [illegible]ed the AC500 in National Carbon air cells and since it had many obvious advantages over the AC500, the CG500 was used for all further work. The maximum [illegible] of operation and, therefore, the maximum electrolyte concentration [illegible] by the heat resistance of the porous carbon electrode in the [illegible] assembly.

[illegible] CONSTRUCTION OF CG500 AIR CELL

The CG500 electrode assembly consisted of a plastic holder containing [illegible] backed porous carbon plates of approximately 25 sq.in. area between two [illegible] Plates I and II, with a 3/8" space between each pair of [illegible]. A space was provided between the carbon plates to allow [illegible] for supplying oxygen to the electrode. The electrolyte used in our [illegible] liters of NaOH. The cell as supplied by National Carbon Co. used [illegible] KOH primarily because its freezing point is lower than that of NaOH.

In order to modify this electrode assembly for oxygen supplied under a [illegible] pressure [illegible] plate was used to seal off the carbon electrodes from

air. Pure oxygen at 1 psig was then supplied from an H_2O_2 generator or an O_2 bottle to the cell. This insured a slight excess of oxygen in most cases. A hole was drilled in one zinc plate to allow for the introduction of a thin zinc strip as a reference electrode.

V. VOLTAGE MEASUREMENT CIRCUIT

The primary measuring instrument in the circuit for voltage measurement, Figure 1, was a Fischer Titrimeter available from previous work. This was essentially a vacuum tube voltmeter having a range of 0 to 1.0 volts and calibrated in .01 volt units. In order to extend the range of the meter, a series of voltages was tapped off two dry cells and used to oppose the measured voltage thus reducing it to less than 1 volt. The following potential measurements could be made with this test set up:

1. Reference zinc vs. oxygen electrode.
2. Cell zinc vs. oxygen electrode
3. Reference zinc vs. cell zinc.
4. Calibration measurement on the dry cells.

VI. CURRENT MEASUREMENT AND CELL LOADING CIRCUIT

The current was measured by a 50 mv milliammeter fitted with [illegible] and 100 ampere shunts, Figure 2. The first three ranges could be changed from a selector switch, but the 100 ampere shunt had to be connected directly to the cell.

The cell was loaded with a series of three variable resistors, ([illegible] ohms). A double pole double throw switch was used to connect the resistors in either series or parallel. The three resistors were used in series for low current loads (up to [illegible] amperes). For high current loads (10 to [illegible] amperes) [illegible] resistors were connected in parallel, and the

other 0.5 ohm resistor was connected in parallel with them. The latter resistor could be used for fine adjustment of the load.

VII. TEST PROCEDURE AND RESULTS

The cell consisting of the electrode assembly and approximately 4 liters of electrolyte in a 4-liter beaker was placed on an electric hot plate. A stirrer was used to insure uniform temperature and electrolyte distribution. Readings were taken as the cell was heating up and as it cooled down.

The following data were obtained:

1. Open circuit voltage of the cell.
2. Open circuit voltage of reference vs. oxygen electrode.
3. Current drawn from the cell.
4. Cell zinc vs. oxygen voltage (cell voltage) for these currents.
5. Reference zinc vs. oxygen voltage (reference voltage) for these currents.
6. Temperature of the cell.

Preliminary tests were run at constant temperature, and plots of cell and reference voltage vs. current were prepared. Above about 4 amperes, these plots were straight lines.

Further tests were run at 3 current levels (6, 10, and 15 amperes), and plots of reference voltage vs. temperature at those levels were prepared, Figures [illegible], 8, 10, and 12. From these curves, a series of lines of reference voltage vs. current for different temperatures were prepared, Figures 5, 7, 9, 11 and 13.

These tests were repeated using six different concentrations of NaOH electrolyte, 20, 30, 40, 50, 60, and 70 per cent by weight, and curves of NaOH concentration vs. reference voltage at 15 amperes loading were prepared for cell temperatures [illegible], and [illegible]°C, Figure 14. Cell voltage variation

with NaOH concentration at temperatures to 80°C were also plotted, Figure 15.

VIII. OPERATING LIMITATIONS OF CELL

During preliminary operation at 100°C, the plastic binder in the carbon electrode softened and tended to pull away from the metal backing. Cell operation was, therefore, limited to 90°C for the bulk of the testing.

In addition, high temperature operation with lower strength electrolytes affected the reproducibility of the data. This was probably the result of penetration of the lower strength electrolyte into the carbon electrode due to destruction of the electrode [illegible]proofing. Operation at temperatures up to 85°C was possible with 20, 30, and 40 per cent NaOH electrolytes, but the affect of the electrolytes on the electrode at these temperatures made the results questionable. Therefore, tests on these 3 lower strength electrolytes were rerun several times and the cell temperature was limited to 85°C.

The results with 70 per cent NaOH also were not reproducible. This was due to the high melting point of this electrolyte (about 65°C). Although the cells were heated by a hot plate to keep the electrolyte molten, the O_2 was supplied directly from a cylinder at room temperature and apparently caused freezing of the 70 per cent NaOH electrolyte on the electrode surface. Readings were, therefore, [illegible] had to be discarded.

The maximum current that could be drawn from the cell was, of course, dependent on the internal resistance of the cell, polarization of the electrodes, and minimum external load that could be applied. The maximum current drawn was [illegible] amperes. The test levels of 6, 10, and 15 amperes were chosen because they [illegible] obtained with all the electrolytes used over the temperature range studied. [illegible] attempt was made to reduce the internal cell resistance by physical [illegible]

The results of identical tests run with different electrodes indicated slight variations between these electrodes; therefore, an entire series of tests was carefully performed on one CG500 electrode. The results of this series, as outlined and discussed herein, should be interpreted as indicating the general effects of temperature and concentration of the electrolyte on the CG500 oxygen electrode.

IX. DISCUSSION OF RESULTS

From the first sets of preliminary tests, it was obvious that operation at high temp[illegible] superior to room temperature operation. Therefore, our efforts were concentrated on obtaining good data at as high a temperature as the CG500 could feasibly operate. The data at low temperatures were, therefore, rather sketchy. The curves for 40, 50, and 60°C on Figure 14 are shown as dashed lines to indicate that the results are more of a qualitative nature.

From Figures 4, 6, 8, 10 and 12, we can see that in all cases, raising the temperature increases the reference voltage of the cell. This is due to a decrease in polarization of the O_2 electrode. There is, also, a decrease in internal resistance of the cell as the temperature is raised which makes the improvement in cell voltage even more marked than the improvement in reference voltage. It can also be seen in Figures 4, 6, 8, 10 and 12 that the rate of change of reference voltage with temperature decreases at higher temperatures for a given strength electrolyte and the rate of change of reference voltage over a given temperature range is greater for stronger electrolytes.

Figure 14 illustrates the effect of concentration and temperature of electrolyte on reference voltage for a given load on the cell. At room temperature, 6 Molar NaOH (20%) was the most suitable electrolyte. The polarization of the cell was less and the conductivity was greater than that for any higher strength electrolyte. As the temperature was increased, the high strength

electrolytes [illegible] rapidly until [illegible] about 70°C there was little difference between [illegible]% and 50% NaOH. At 70°C, the 60% NaOH electrolyte gave the highest reference voltage of any of the electrolytes tested, and the curves indicated that even higher strength electrolytes might be an improvement. This was confirmed, to some extent, by the brief tests on [illegible]% NaOH, although reproducible results could not be obtained for reasons discussed above.

In this series of tests, the cell voltage decreased with increased NaOH concentration for 15 amperes load at all temperatures, Figure 15. However, the slope of these curves reduced as the temperature increased, indicating that the electrolyte conductivity increased with temperature at a greater rate as the electrolyte concentration increased. The internal cell resistance was so great however, that the increased conductivity and the reduced polarization of the electrode were insufficient to raise the cell voltage for 60% NaOH at 80°C above that for 20% NaOH at the same temperature despite the fact that in the case of the reference voltage the reverse was true.

X CONCLUSIONS

These results showed that:

(1) High temperature operation reduced both polarization and internal resistance of [illegible] cell utilizing an oxygen electrode.

(2) The use of highly concentrated electrolyte also reduced polarization [illegible]

(3) There was an optimum electrolyte concentration for minimum internal resistance of the cell for a given operating temperature.

[illegible] it [illegible] concluded that use of concentrated electrolyte and [illegible] temperature can result in increased capacity of the oxygen electrode. [illegible] extent of such increase in a practical cell will be dependent on [illegible]

Work reported elsewhere by the National Carbon Co. resulted in a similar beneficial effect on an oxygen electrode when pressure is increased. Therefore, [illegible]re, high pressure cell might be constructed which would have high [illegible]ity. Such a cell using oxygen from the decomposition of H_2O_2 combined with a [illegible] engine operating on the heat of decomposition of the H_2O_2 should yield a very [illegible] [illegible]lsion system. The cell could also be operated on air when air is available.

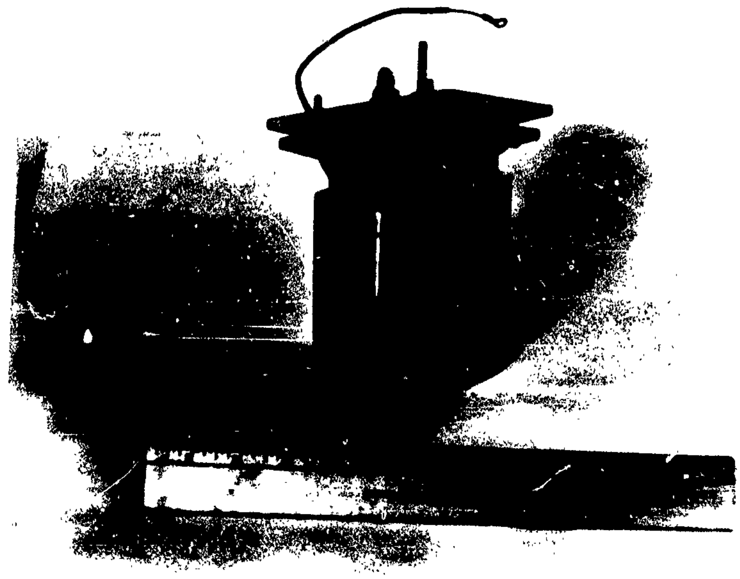


PLATE 1

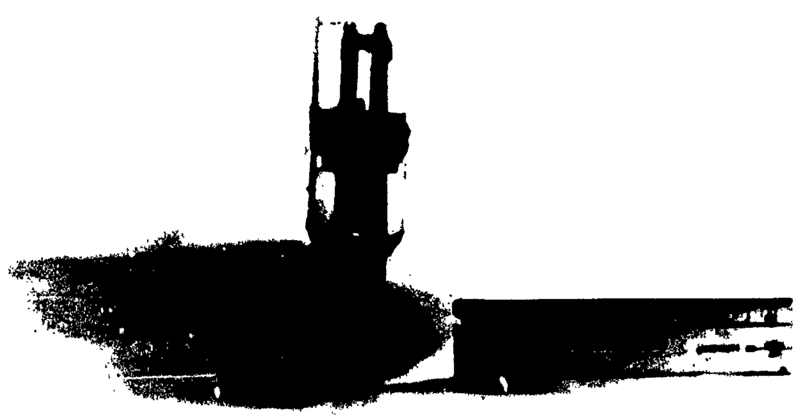
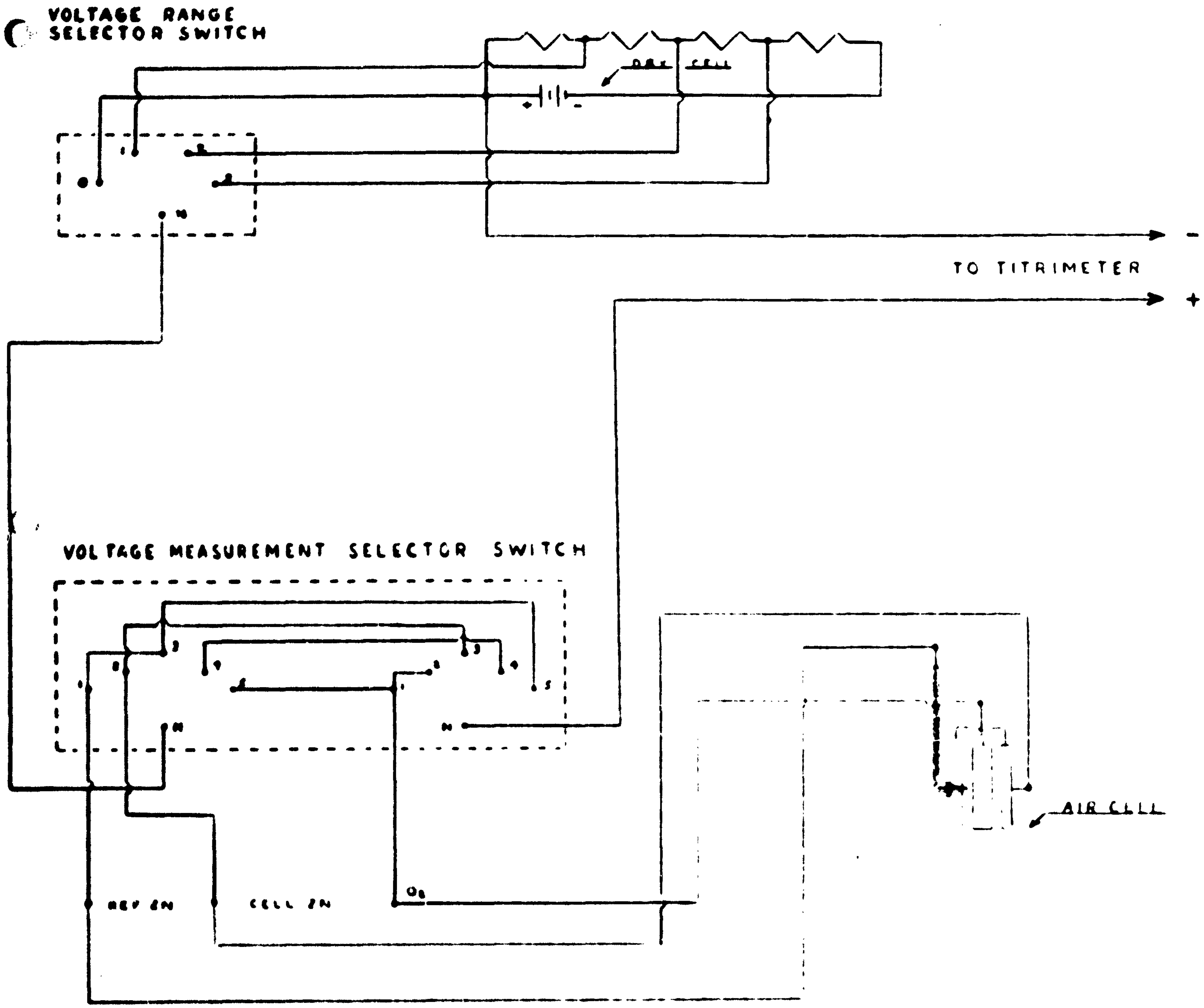


PLATE 2

CF-10 Air Cell Electrode Assembly

VOLTAGE MEASURING CIRCUIT

F-1



TWO WAFER SELECTOR SWITCH

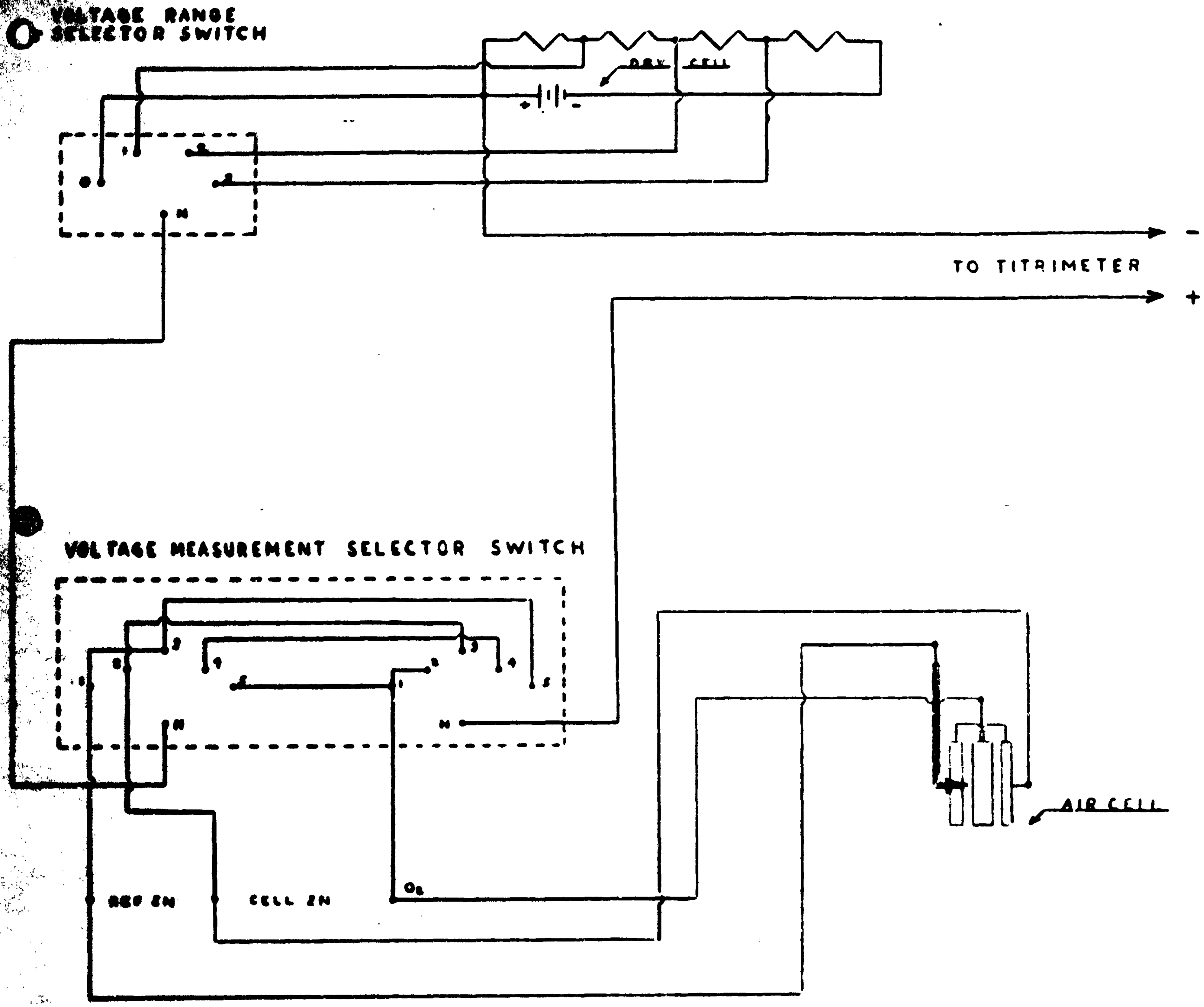
POS.	MEASUREMENT
1	REF - OXYGEN
2	ZINC - OXYGEN
3	REF - ZINC
4	CALIBRATE DRY CELL
5	OXG - REF

THREE POSITION SELECTOR SWITCH

NO 0 - OFF 0 - 1.000
NO. 1 - .762 VOLT .762 - 1.762
NO. 2 - 1.530 " 1.530 - 2.530
NO 3 - 2.281 " 2.281 - 3.281

VOLTAGE MEASURING CIRCUIT

FIG 1



TWO WAFER SELECTOR SWITCH

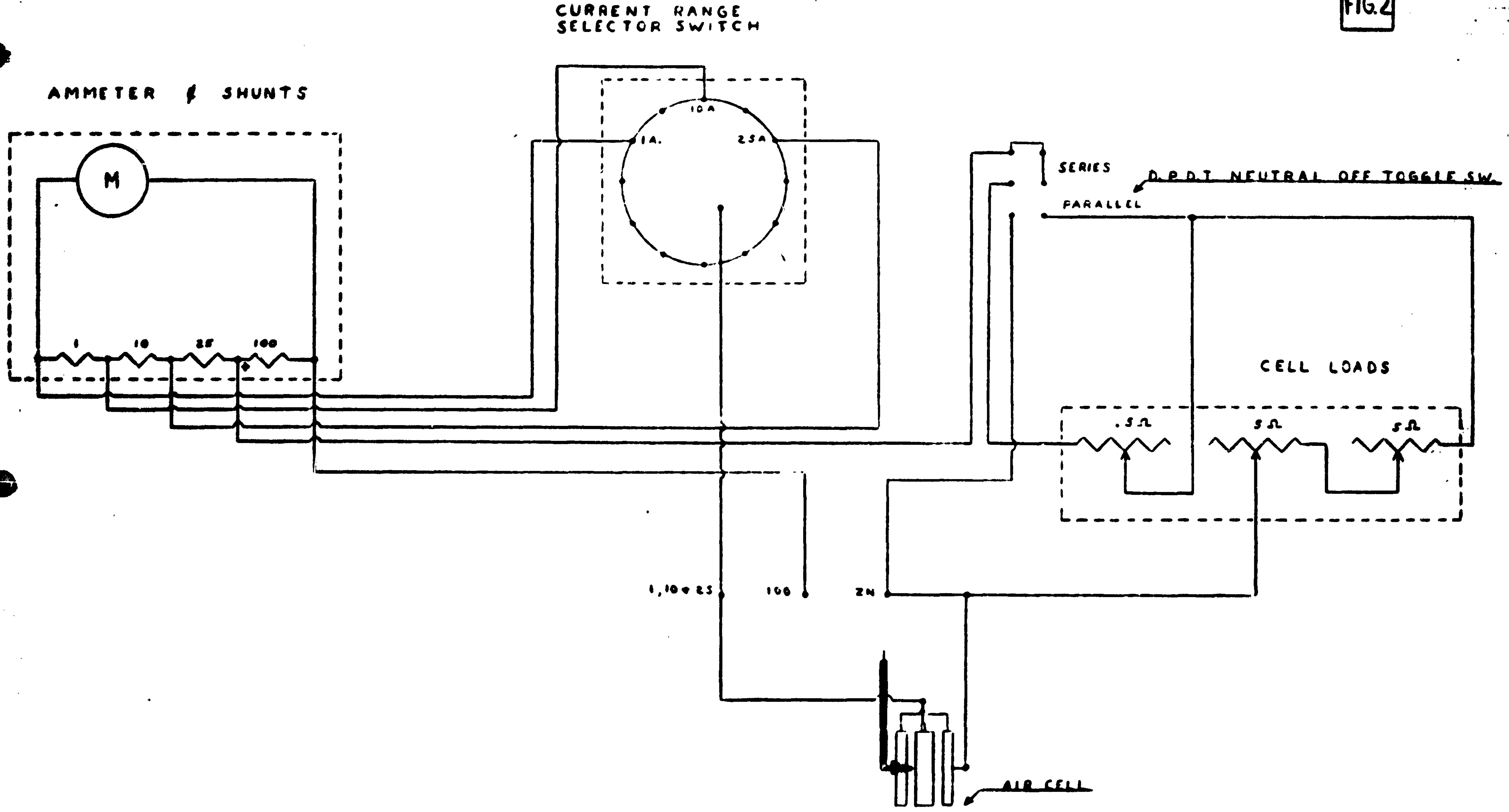
POS.	MEASUREMENT
1	REF - OXYGEN
2	ZINC - OXYGEN
3	REF - ZINC
4	CALIBRATE DRY CELL
5	OXG - REF

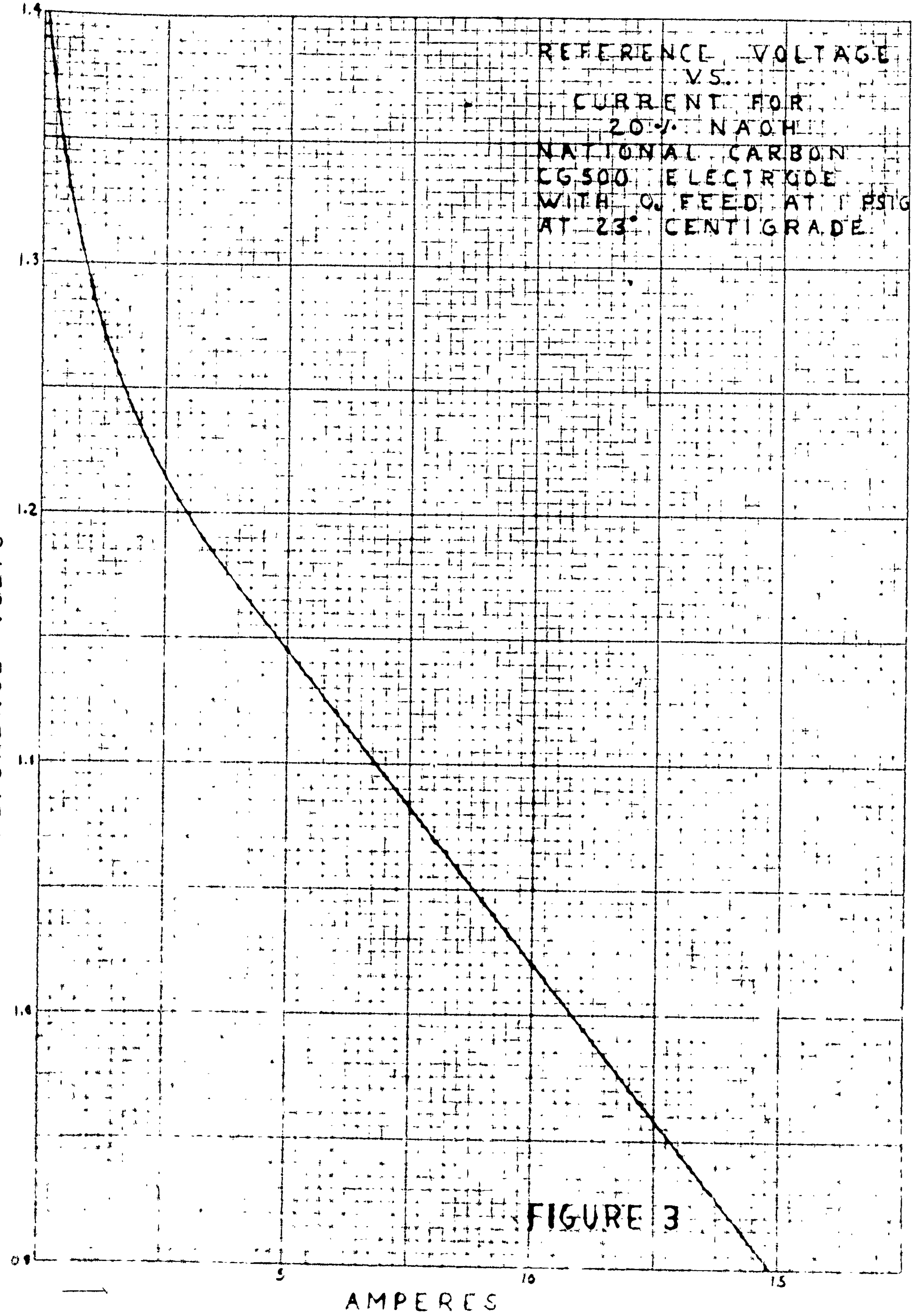
THREE POSITION SELECTOR SWITCH

NO. 0 -	OFF		0 - 1.000
NO. 1 -	.762	VOLT	.762 - 1.762
NO. 2 -	1.530	"	1.530 - 2.530
NO. 3 -	2.281	"	2.281 - 3.281

CURRENT MEASURING CIRCUIT

FIG.2




REFERENCE VOLTAGE VS. CURRENT FOR 20% NAOH NATIONAL CARBON CG500 ELECTRODE WITH O2 FEED AT 1 PSIG AT 23° CENTIGRADE
REFERENCE VOLTS
AMPERES
1.4
1.3
1.2
1.1
1.0
0.9
5
10
15
FIGURE 3

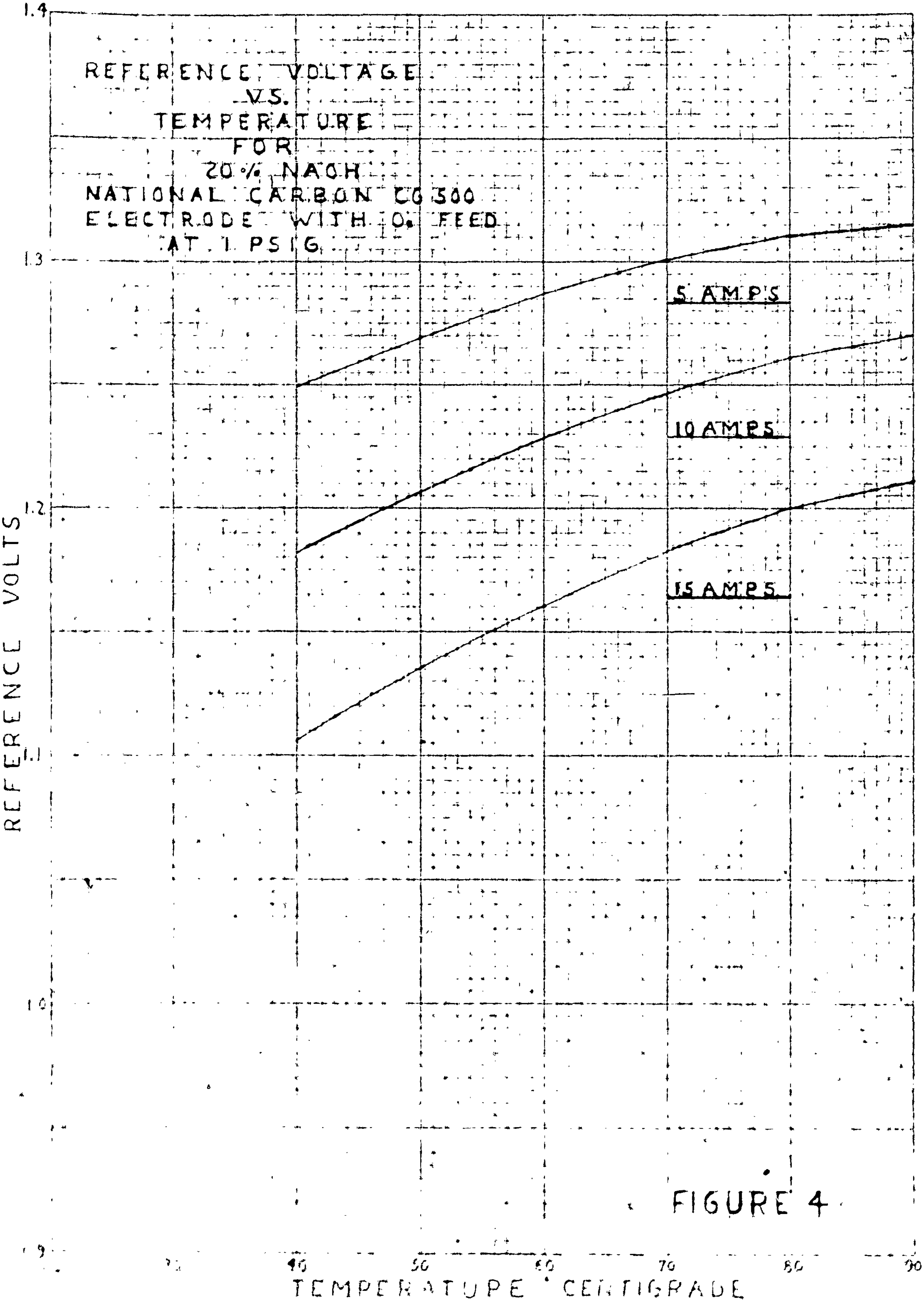

REFERENCE VOLTAGE
VS.
TEMPERATURE
FOR
20% NAOH
NATIONAL CARBON CG 300
ELECTRODE WITH O₂ FEED
AT 1 PSIG
5 AMPS
10 AMPS
15 AMPS
REFERENCE VOLTS
TEMPERATURE CENTIGRADE
1.4
1.3
1.2
1.1
1.0
.9
40
50
60
70
80
90

FIGURE 4

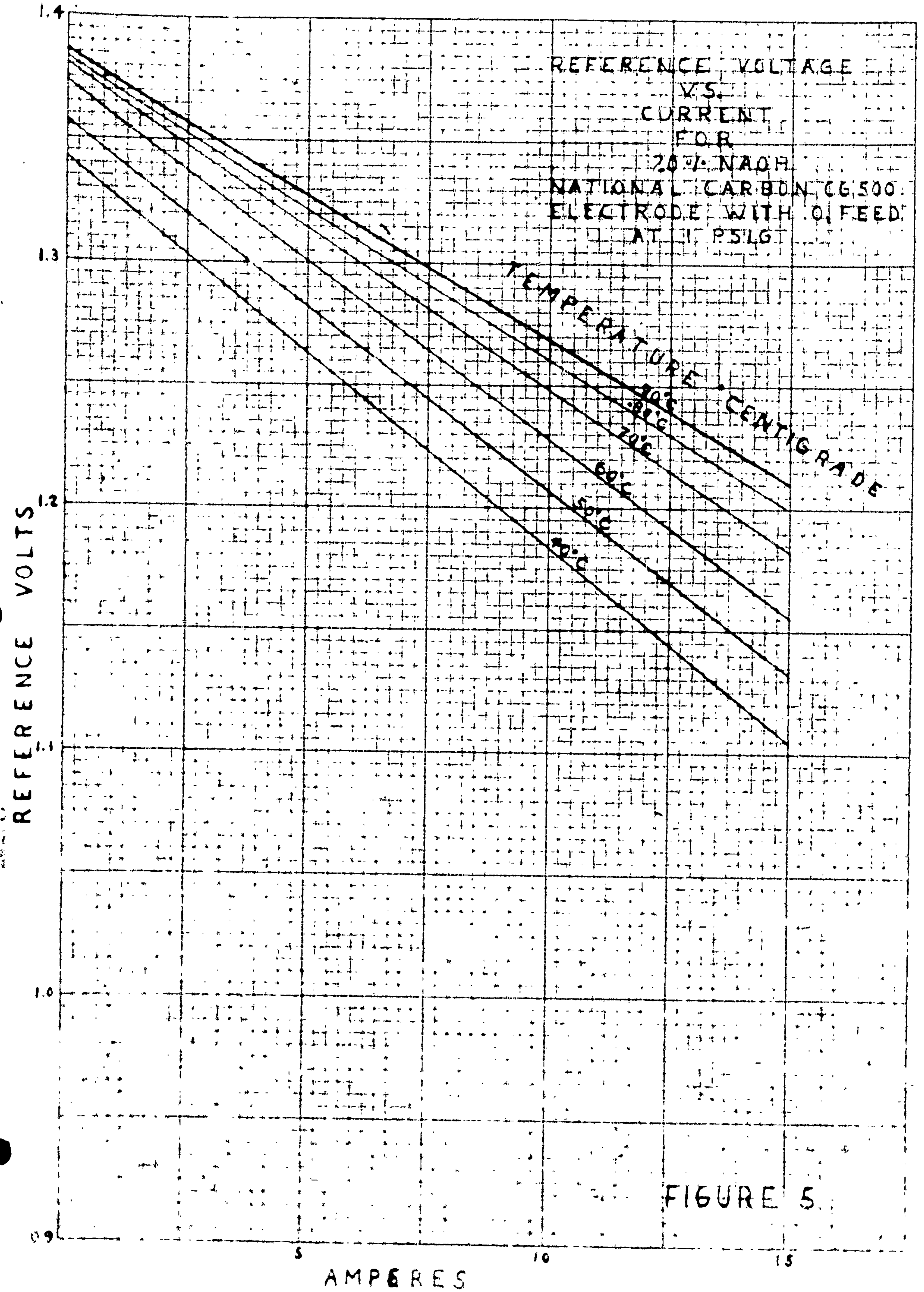

REFERENCE VOLTAGE
V.S.
CURRENT
FOR
20% NAOH
NATIONAL CARBON CG 500
ELECTRODE WITH O_2 FEED
AT 1 PSIG
TEMPERATURE CENTIGRADE
90°C
80°C
70°C
60°C
50°C
40°C
1.4
1.3
1.2
1.1
1.0
0.9
5
10
15
REFERENCE VOLTS
AMPERES

FIGURE 5

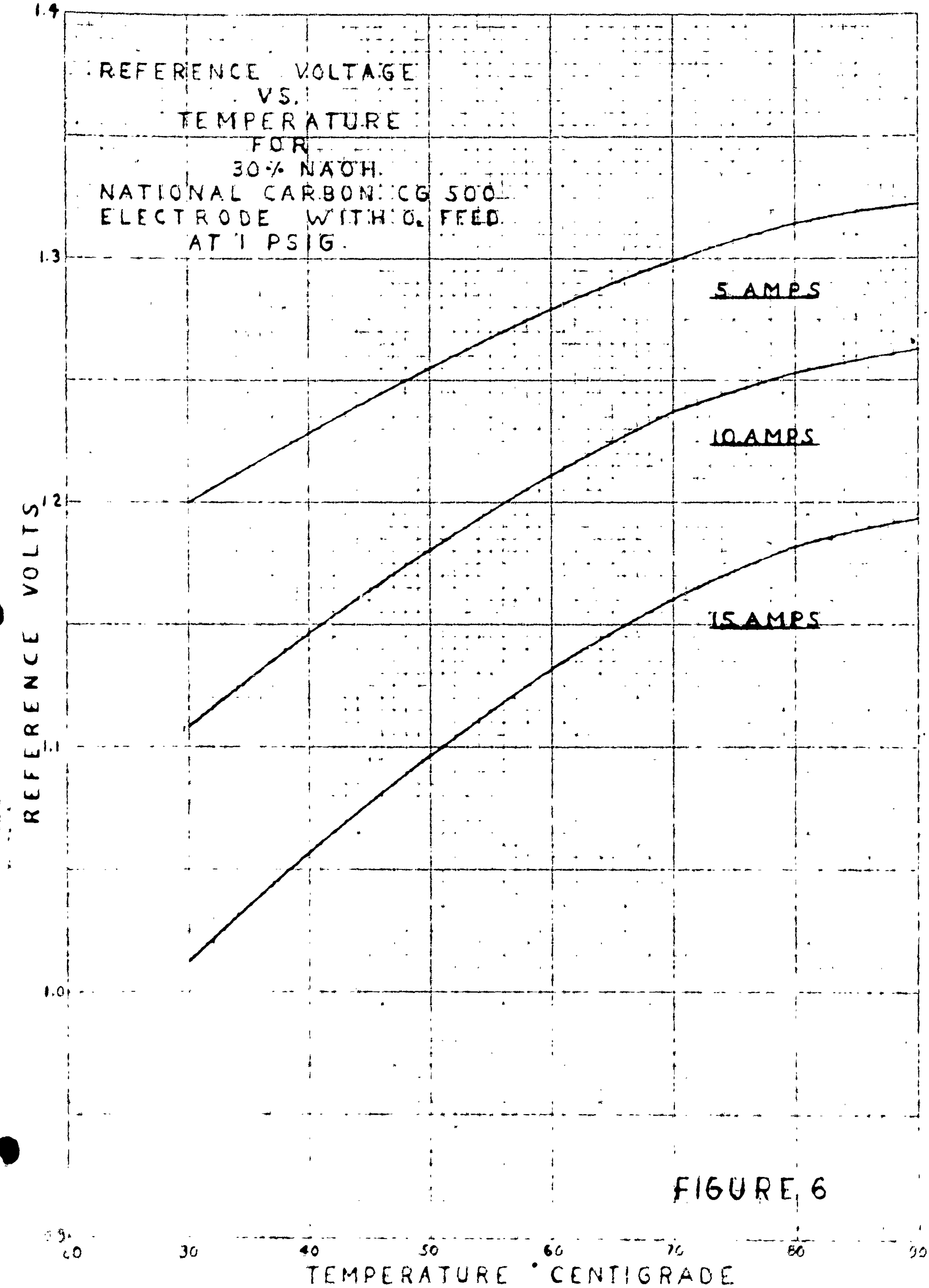
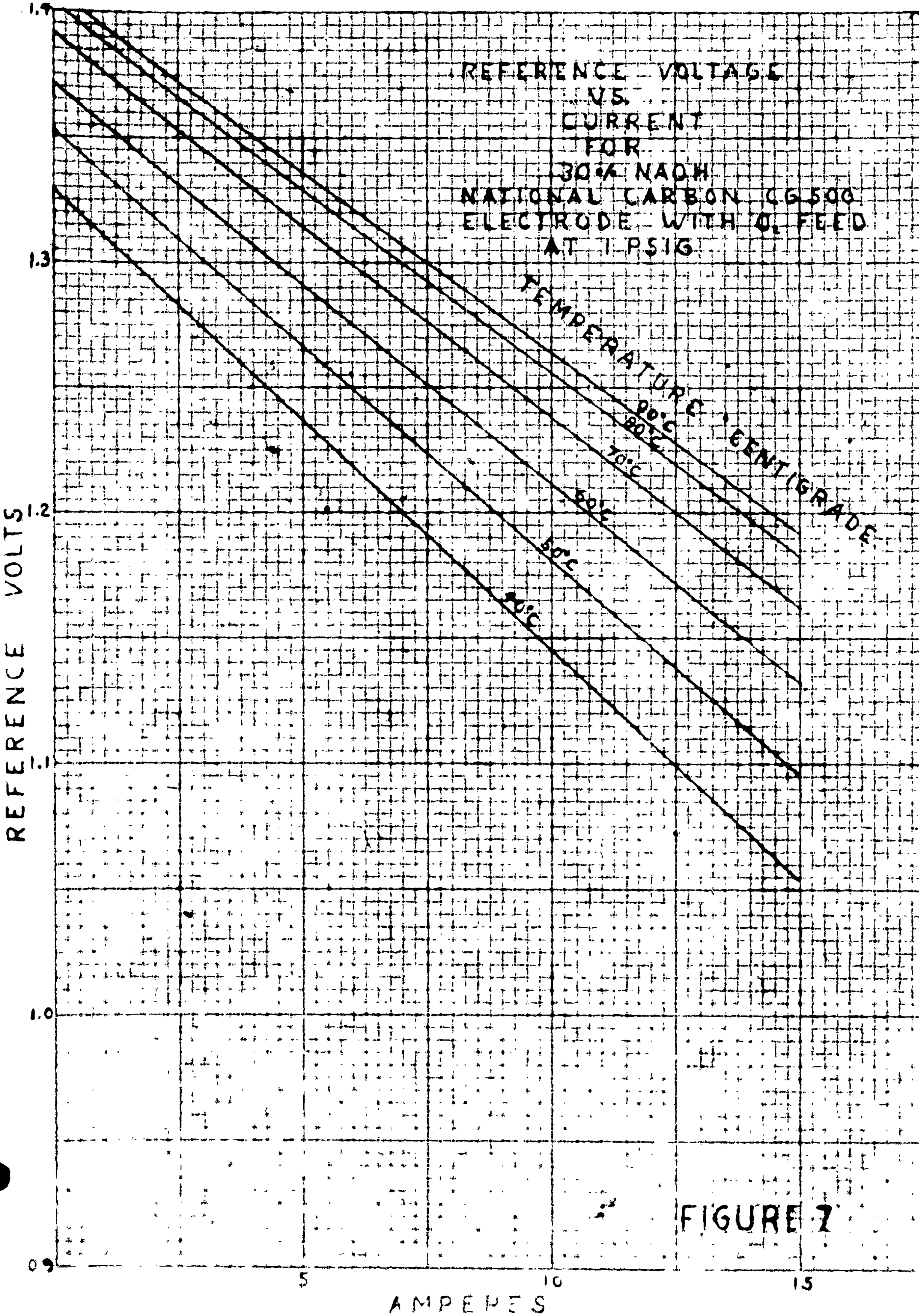

REFERENCE VOLTAGE
VS.
TEMPERATURE
FOR
30% NAOH
NATIONAL CARBON CG 500
ELECTRODE WITH O_2 FEED
AT 1 PSIG
5 AMPS
10 AMPS
15 AMPS
REFERENCE VOLTS
TEMPERATURE CENTIGRADE
1.4
1.3
1.2
1.1
1.0
.9
20
30
40
50
60
70
80
90

FIGURE 6



REFERENCE VOLTAGE
VS.
CURRENT
FOR
30% NAOH
NATIONAL CARBON CG500
ELECTRODE WITH O2 FEED
AT 1 PSIG
TEMPERATURE CENTIGRADE
90°C
80°C
70°C
60°C
50°C
40°C
REFERENCE VOLTS
AMPERES
1.4
1.3
1.2
1.1
1.0
0.9
5
10
15

FIGURE 7

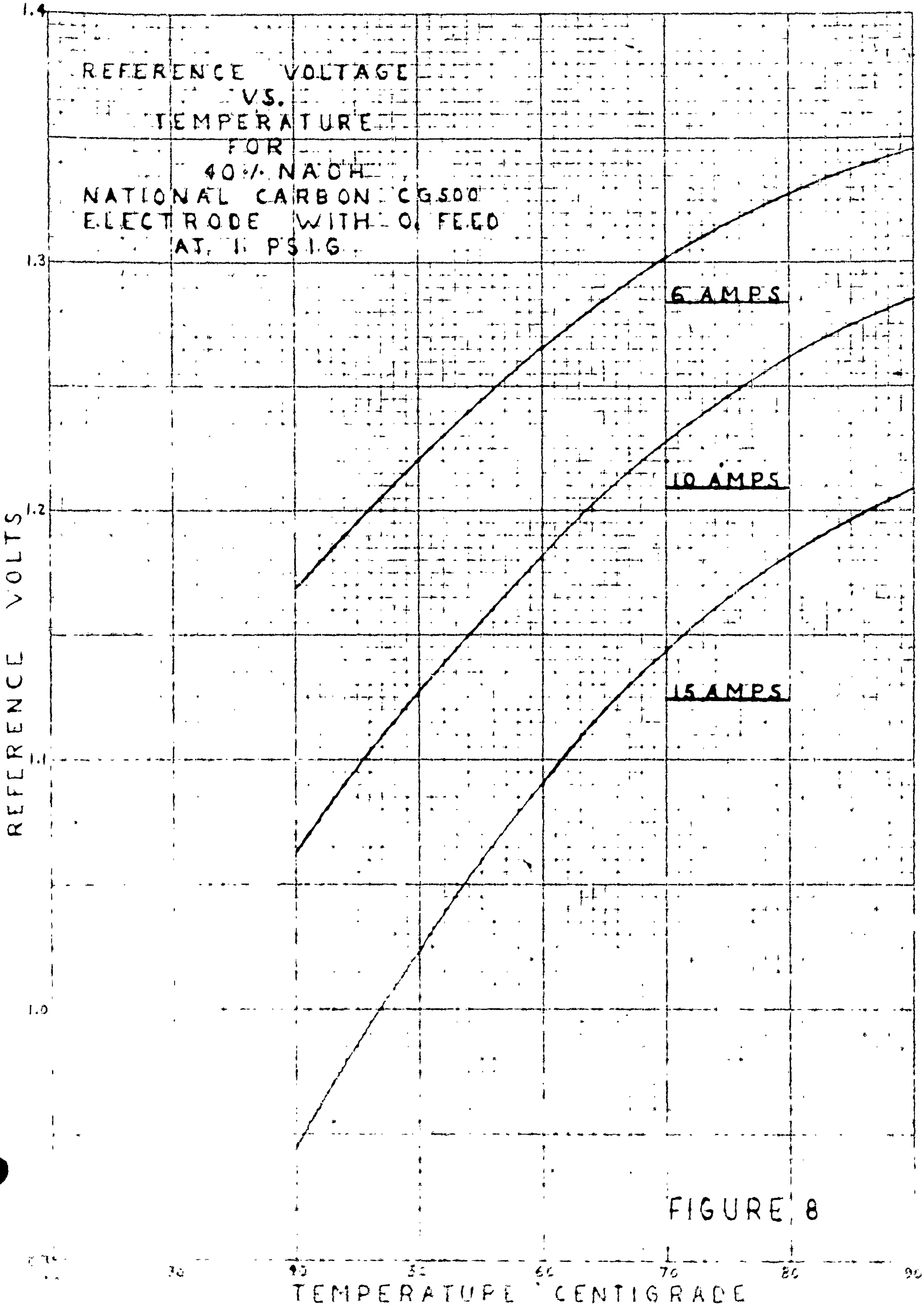

REFERENCE VOLTAGE
VS.
TEMPERATURE
FOR
40% NAOH
NATIONAL CARBON CG500
ELECTRODE WITH O2 FEED
AT 1 PSIG
6 AMPS
10 AMPS
15 AMPS
REFERENCE VOLTS
TEMPERATURE CENTIGRADE
1.4
1.3
1.2
1.1
1.0
30
40
50
60
70
80
90

FIGURE 8

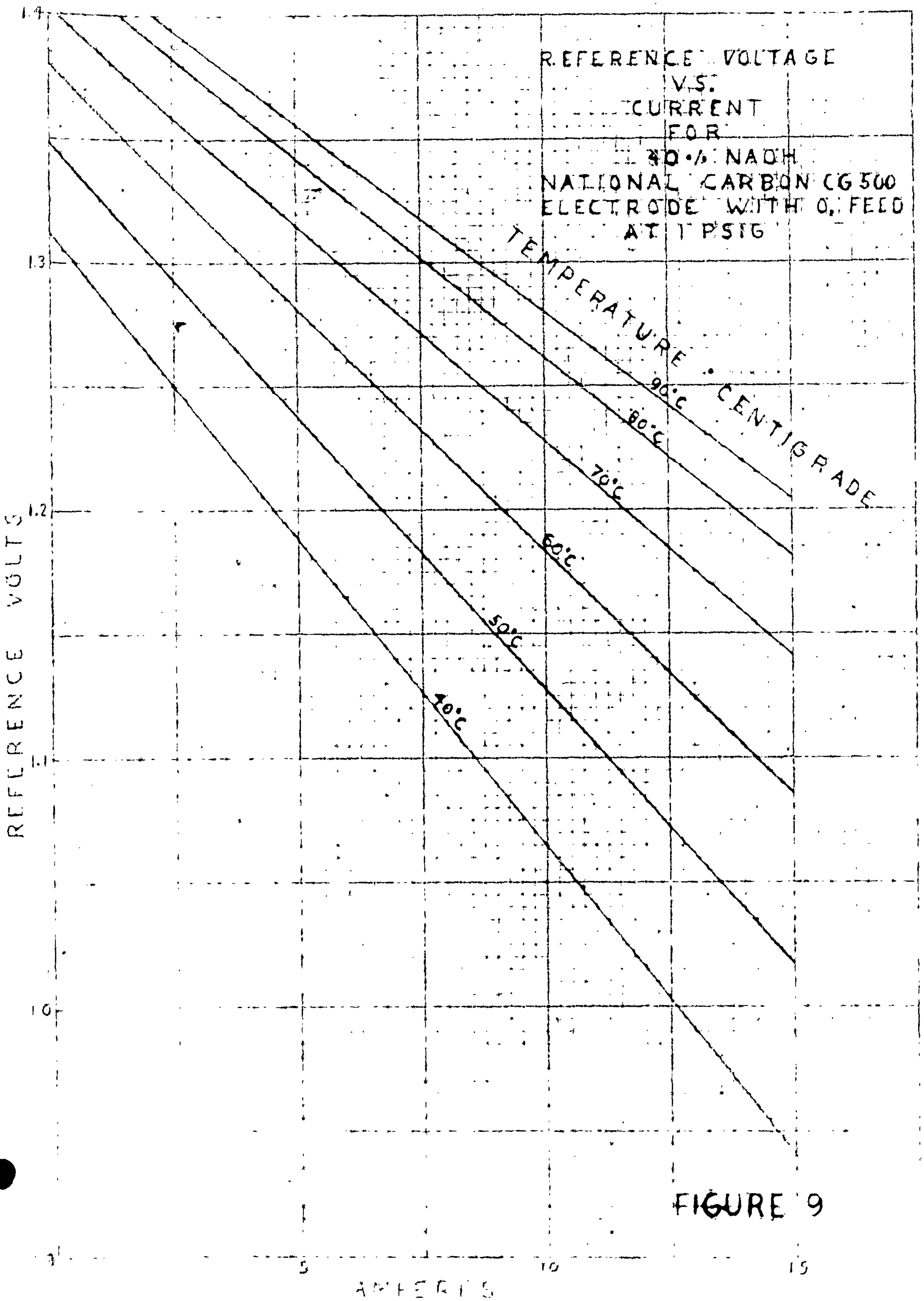
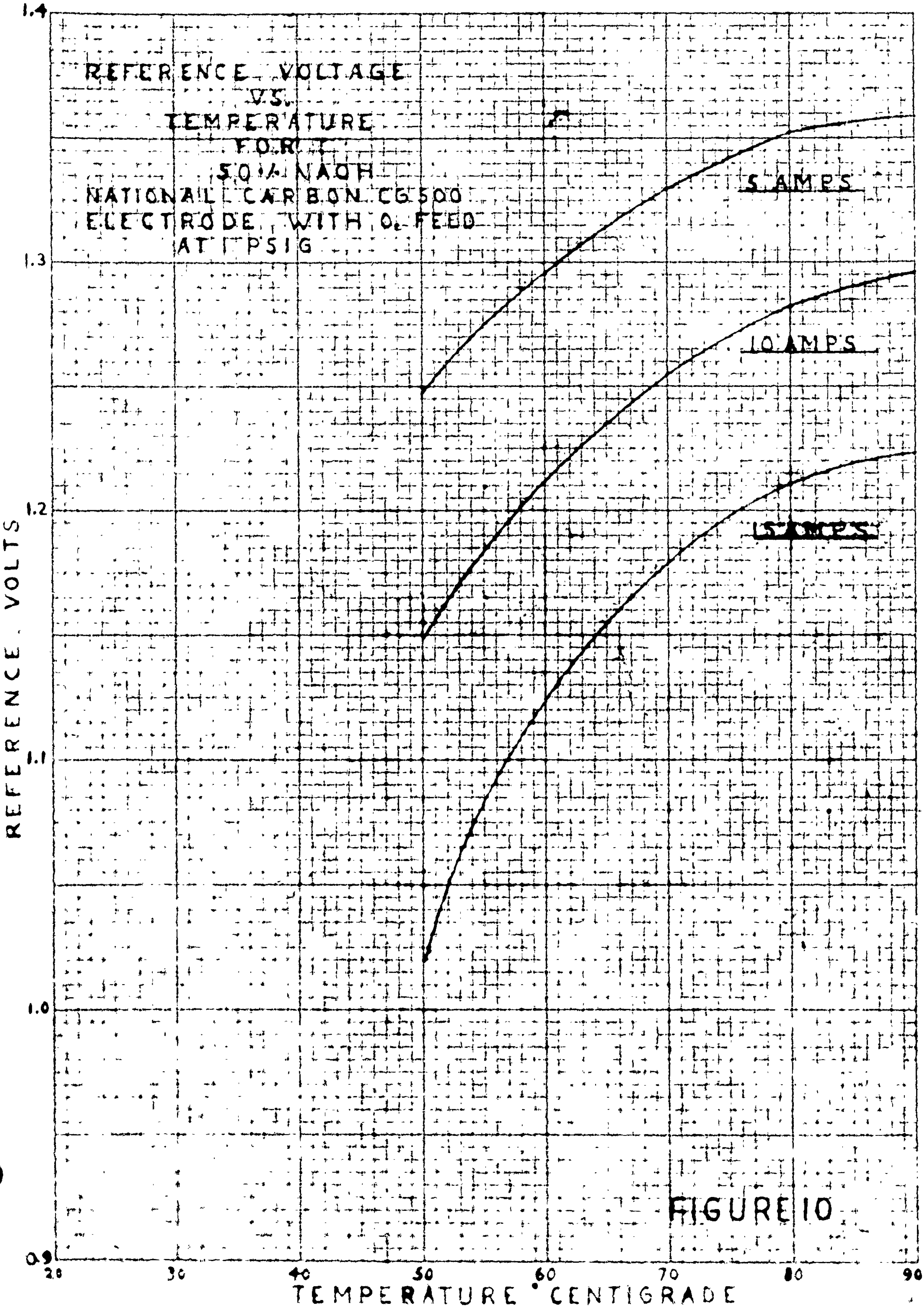
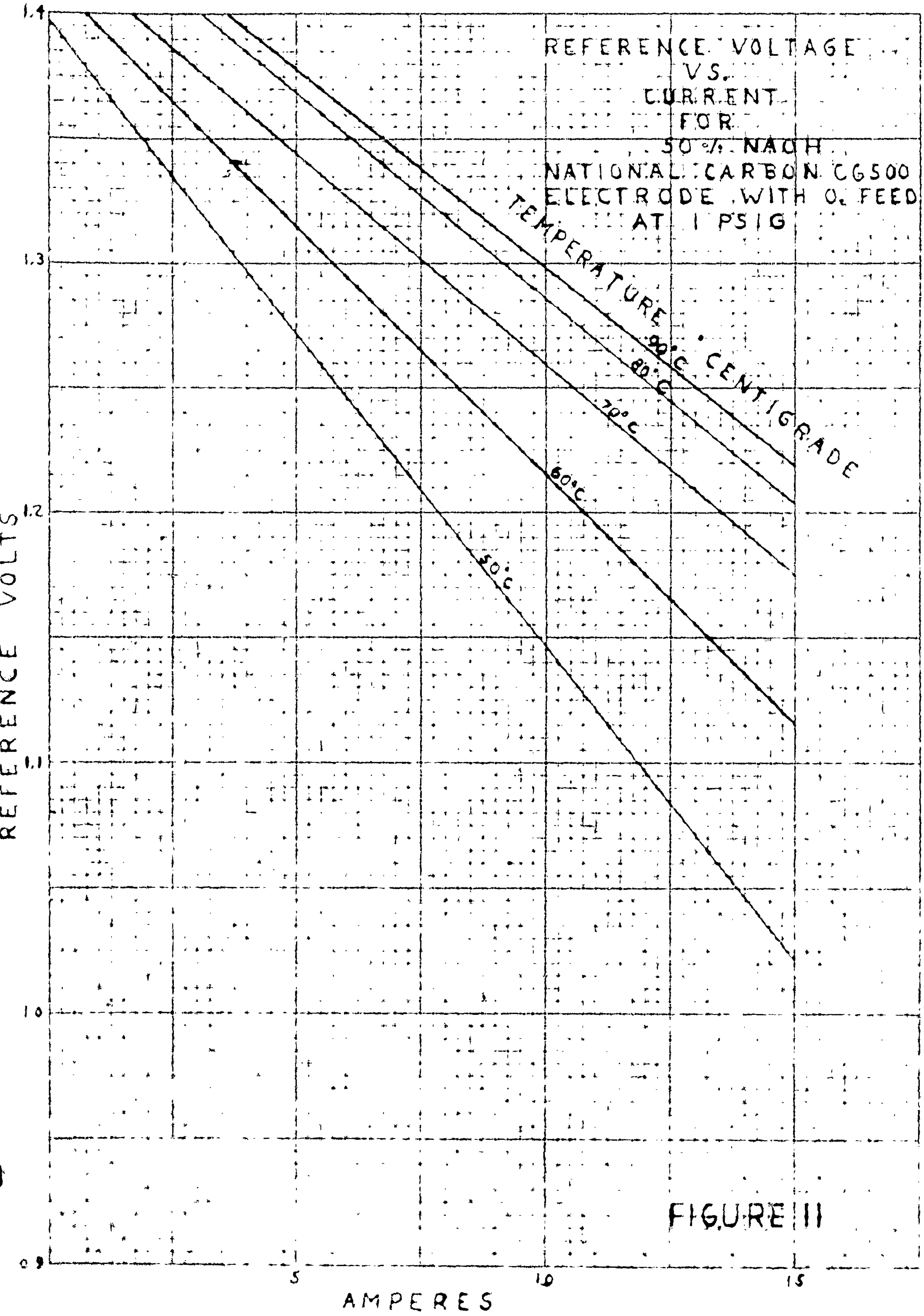

REFERENCE VOLTAGE
V.S.
CURRENT
FOR
40% NAOH
NATIONAL CARBON CG 500
ELECTRODE WITH O_2 FEED
AT 1 PSIG
TEMPERATURE . CENTIGRADE
90°C
80°C
70°C
60°C
50°C
40°C
REFERENCE VOLTS
1.4
1.3
1.2
1.1
1.0
5
10
15
AMPERES

FIGURE 9



REFERENCE VOLTAGE
VS.
TEMPERATURE
FOR
50% NAOH
NATIONAL CARBON CG500
ELECTRODE WITH O2 FEED
AT 1 PSIG
5 AMPS
10 AMPS
15 AMPS
REFERENCE VOLTS
TEMPERATURE CENTIGRADE
1.4
1.3
1.2
1.1
1.0
0.9
20
30
40
50
60
70
80
90

FIGURE 10


REFERENCE VOLTAGE
VS.
CURRENT
FOR
50% NAOH
NATIONAL CARBON CG500
ELECTRODE WITH O_2 FEED
AT 1 PSIG
TEMPERATURE, CENTIGRADE
90°C
80°C
70°C
60°C
50°C
REFERENCE VOLTS
AMPERES
1.4
1.3
1.2
1.1
1.0
0.9
5
10
15
FIGURE 11

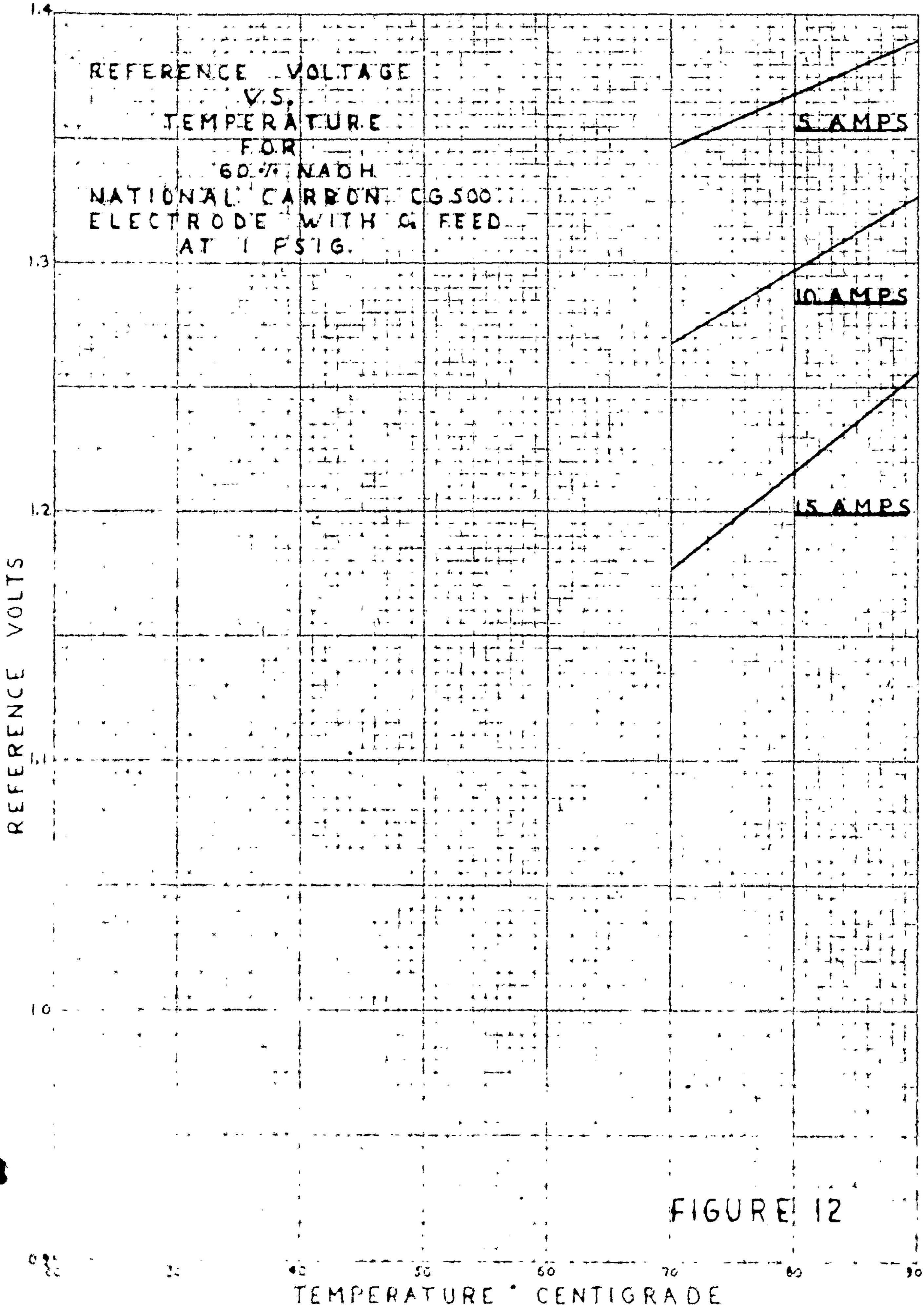

REFERENCE VOLTAGE
V.S.
TEMPERATURE
FOR
60% NAOH
NATIONAL CARBON CG500
ELECTRODE WITH C FEED
AT 1 PSIG.
5 AMPS
10 AMPS
15 AMPS
REFERENCE VOLTS
TEMPERATURE ° CENTIGRADE
1.4
1.3
1.2
1.1
1.0
40
50
60
70
80
90

FIGURE 12

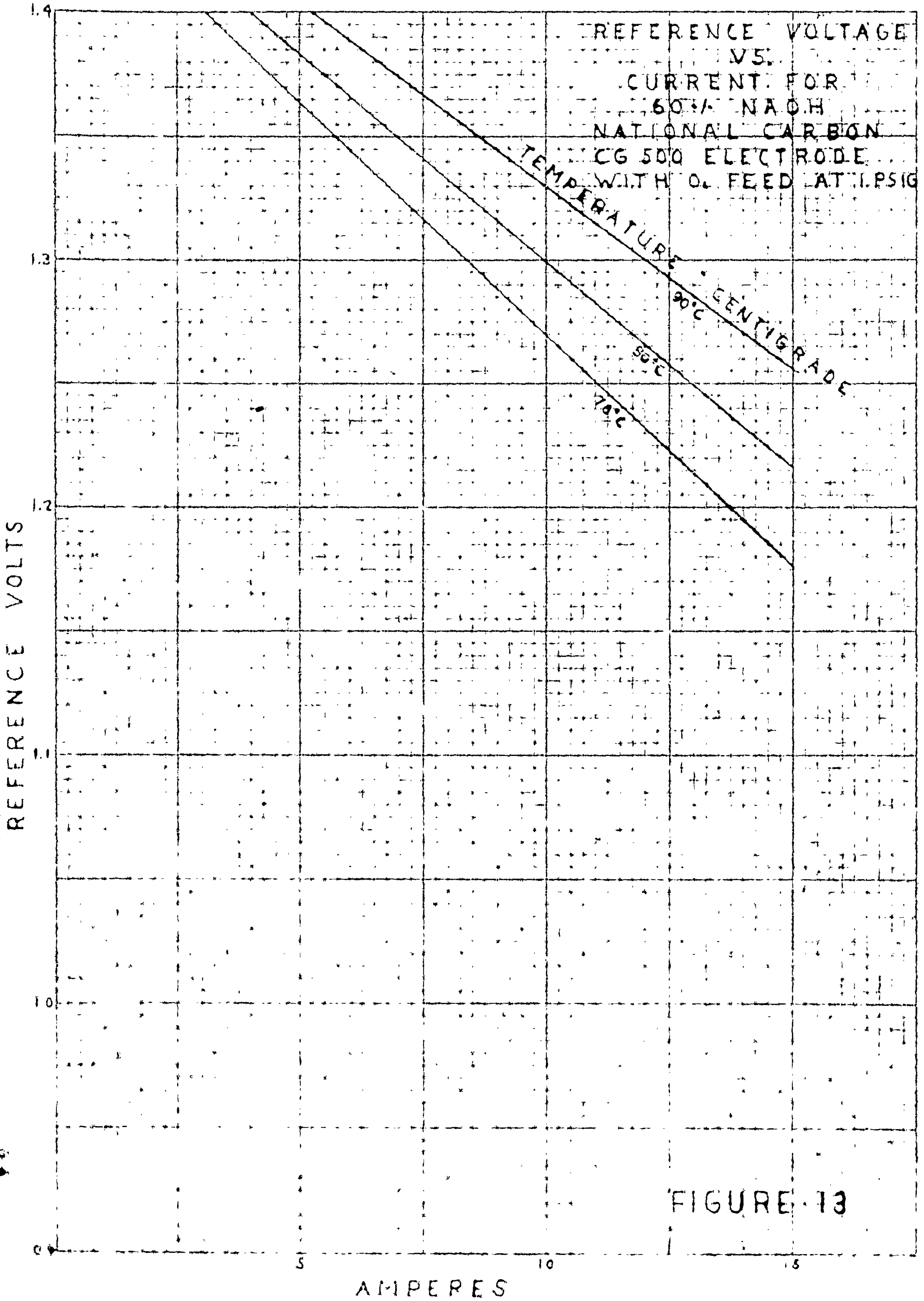
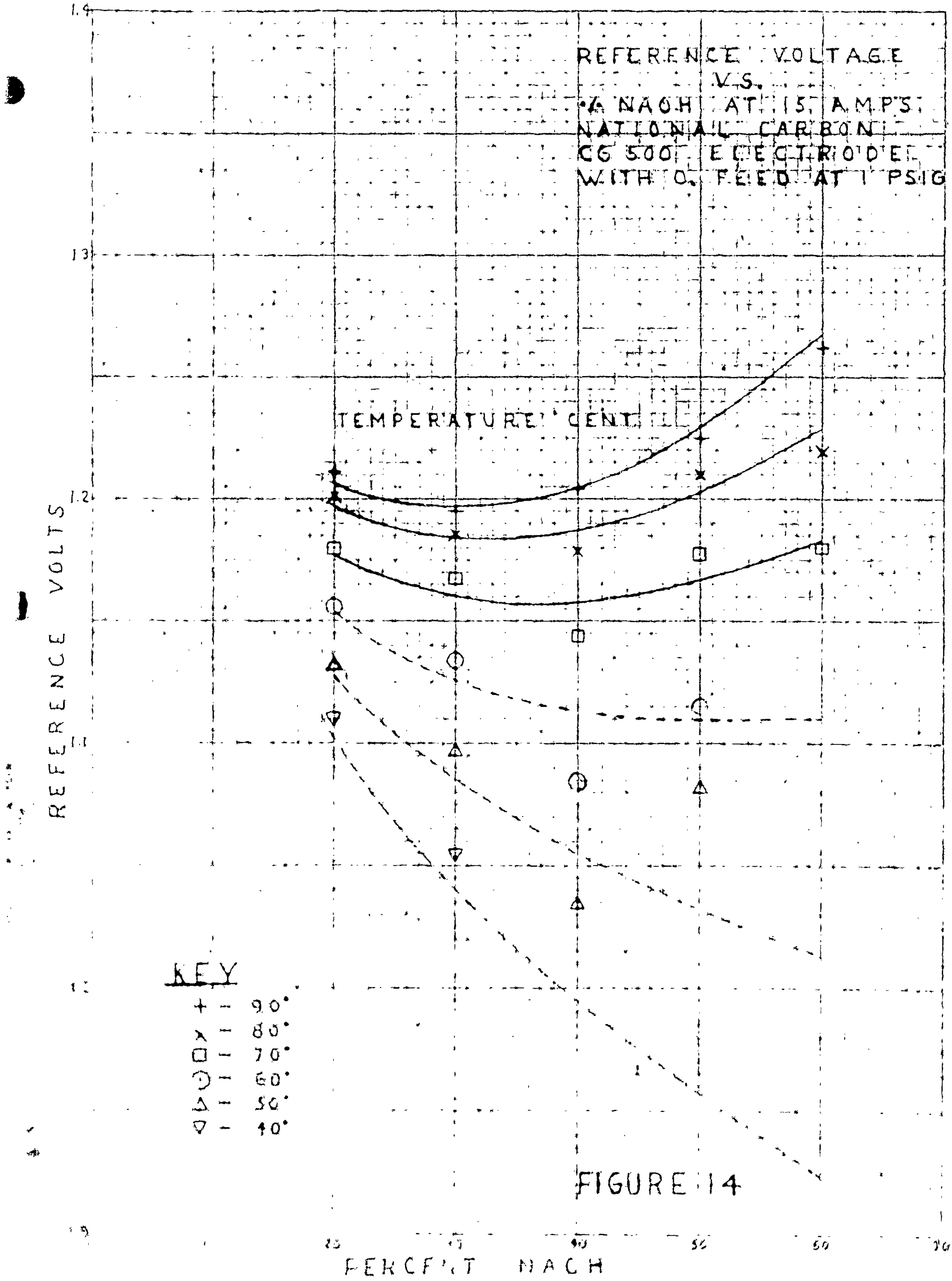

REFERENCE VOLTAGE
VS.
CURRENT FOR
60% NAOH
NATIONAL CARBON
CG 500 ELECTRODE
WITH O₂ FEED AT 1 PSIG
TEMPERATURE · CENTIGRADE
90°C
80°C
70°C
REFERENCE VOLTS
AMPERES
1.4
1.3
1.2
1.1
1.0
0.9
5
10
15

FIGURE 13



REFERENCE VOLTAGE
VS.
% NAOH AT 15 AMPS
NATIONAL CARBON
CG 500 ELECTRODE
WITH O_2 FEED AT 1 PSIG
TEMPERATURE CENT.
KEY
+ - 90°
x - 80°
□ - 70°
○ - 60°
△ - 50°
▽ - 40°
REFERENCE VOLTS
PERCENT NACH
1.4
1.3
1.2
1.1

FIGURE 14

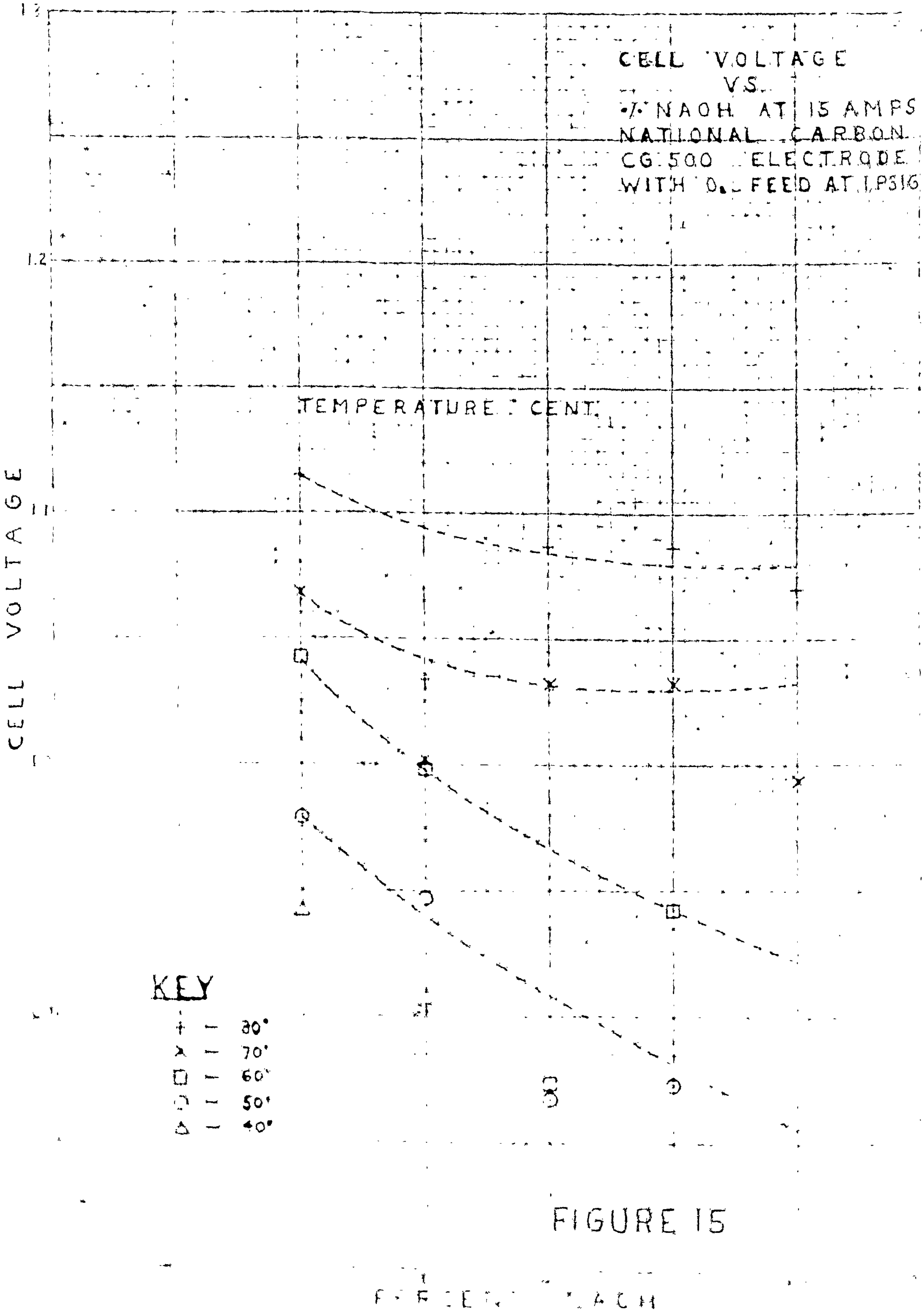

CELL VOLTAGE
V.S.
% NAOH AT 15 AMPS
NATIONAL CARBON
CG 500 ELECTRODE
WITH O2 FEED AT 1 PSIG
1.2
TEMPERATURE CENT.
CELL VOLTAGE
KEY
+ — 80°
x — 70°
□ — 60°
○ — 50°
△ — 40°

FIGURE 15